Electronic Correlations in CoO_2, the Parent Compound of Triangular Cobaltates

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A ^{59}Co NMR study of CoO_2, the $x = 0$ end member of A_xCoO_2 (A=Na, Li...) cobaltates, reveals a metallic ground state, though with clear signs of strong electron correlations: low-energy spin fluctuations develop at wave vectors $q \neq 0$ and a crossover to a Fermi-liquid regime occurs below a characteristic temperature $T^* \simeq 7$ K. Despite some uncertainty over the exact cobalt oxidation state in this material, the results show that electronic correlations are revealed as x is reduced below 0.3. The data are consistent with Na_xCoO_2 being close to the Mott transition in the $x \to 0$ limit.

Doping a Mott insulator (a state where electrons are forced to localize by Coulomb repulsion U) with charge carriers can lead to a variety of strongly correlated electronic phases with outstanding properties such as d-wave superconductivity or colossal magnetoresistance [1]. Recently, studies of sodium cobalt oxides Na_xCoO_2 have revealed a rich phase diagram with superconductivity, anomalous magnetism and strong thermopower. A large number of theoretical attempts to explain these phenomena are based on the infinite-U limit of the Hubbard Hamiltonian, the t-J model. In this approach, sodium cobaltates are triangular analogs of (electron doped) cuprate superconductors and the "undoped" $x = 0$ phase CoO_2 should be a Mott insulator.

The doped Mott insulator picture is, however, challenged by the experimental observation that Na_xCoO_2 appears to become a less and less correlated metal as x is reduced from ∼0.7 down to 0.18 (if one excepts the singular $x = 0.5$ composition) [2]. This raises a two-fold question: Is the ground state of CoO_2 metallic or insulating [3]? If metallic, how far is CoO_2 from the Mott transition, which is predicted to occur at $U/|t| \simeq 10.5 - 12$ for the Hubbard model on a triangular lattice [4]? In other words, how strong are electron correlations in CoO_2?

The $x = 0$ limit is not just theoretical: In 1996, Amatucci, Tarascon and Klein discovered that a well-defined (O1) phase forms right at $x = 0$ after full electrochemical delithiation of Li_xCoO_2 [5, 6]. This phase, which is not stable in air, has since been reproduced by several groups [7, 8]. From the structural point of view, the CoO_2 blocks are identical to those in Li_xCoO_2 or Na_xCoO_2. The c-axis parameter is somewhat contracted, but the in-plane Co-Co distance is almost unchanged. Furthermore, the stoichiometric nature of this phase is manifested in the established phase separation with the adjacent H1-3 phase ($Li_{0.12}CoO_2$) [7]. CoO_2 is thus the ideal candidate for studying the strategic $x = 0$ limit of triangular cobaltates.

In this Letter, we report the bulk and local magnetic properties of CoO_2 using magnetization and ^{59}Co NMR data. CoO_2 is found to be a metal rather than an insulator. Nevertheless, the evidence for spin fluctuations

and for a Fermi liquid regime occurring at much lower temperature (T) than in $Na_{0.3}CoO_2$ highlight the vigor of electron correlation and the probable closeness to the Mott transition.

Polycrystalline CoO_2 samples were obtained by oxidizing stoichiometric $LiCoO_2$ as the positive electrode material in Swagelok type cells charged to 5.1 V. The cells were assembled in an argon filled glove box with lithium metal as the negative electrode and a borosilicate glass fiber sheet saturated with 1 M $LiPF_6$ in sulfone (Merck) as the electrolyte. The composite positive electrode was prepared by mixing 80 wt.% active material with 20 wt.% acetylene black. The X-ray diffraction (XRD) pattern of the synthesized powder, recorded in an atmosphere-controlled chamber, displays the sharp peaks typical of crystalline CoO_2 (Inset to Fig. 2a). The refined cell parameters are $a = b = 2.806(1)$ Å, $c = 4.313(4)$ Å (space group P-3m). The peak at $2\theta = 19.65°$, also reported by other groups, is attributed to the Li-rich H1-3 phase [7].

Samples (∼40 mg) were placed under an inert atmosphere inside a sealed quartz tube, in order to prevent any exposure to air. Degradation of CoO_2 was ruled out by XRD measurements performed after the NMR experiment. Reproducible NMR results were obtained from three different samples. We have checked that the samples exposed to air showed, in contrast to CoO_2, a large distribution of nuclear relaxation rates extending to much longer values, as well as spectra with significantly lower shifts and unresolved quadrupolar structure.

^{59}Co NMR spectra recorded at different magnetic field values in randomly oriented powders provide a powerful way to distinguish the two phases seen in XRD: In a field of ∼13.5 T, the difference between the high field side of the NMR spectrum and the simulation with a single cobalt site (grey area in Fig. 1) reveals a contribution which is hardly detectable at lower fields because of its larger overlap with the main signal. This secondary signal, which is small (18 % of the total ^{59}Co intensity) and broad (no quadrupolar splitting is resolved), can be singled out at T=200 K: At this T, the main signal almost vanishes because it has a shorter spin-spin relaxation time T_2. The lower hyperfine shift shows that the
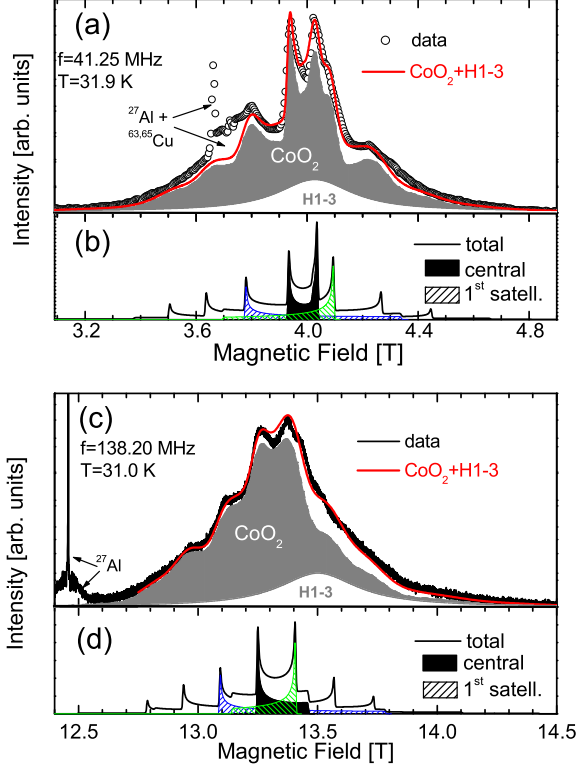
FIG. 1: (a) and (c): ^{59}Co NMR powder spectra at two different frequency values and the simulated spectra with two components (see text). Spurious ^{27}Al and ^{63,65}Cu signals come from the NMR probe. (b) and (d) Corresponding simulations of the CoO$_2$ signal without broadening. For both frequencies, the lower-field peak corresponds to the central transition of grains oriented with $H\|ab$ (see text). For $H \sim 13$ T, the higher-field peak is mainly the $H\|ab$ part of the first quadrupolar satellite. For $H \sim 4$ T, this peak is primarily caused by the second order quadrupolar shift on the central line.

secondary signal comes from less magnetic cobalt ions. All these elements suggest that this signal corresponds to the H1-3 phase evidenced in XRD data.

The main signal, attributed to the CoO$_2$ phase, has an asymmetrical shape which is explained by a strong magnetic shift anisotropy. Since the local symmetry at Co sites is the same as in A$_x$CoO$_2$, we assume axial magnetic symmetry around the c axis, which is also the direction of the principal axis of the electric field gradient, as in all other Na$_x$CoO$_2$ compounds [9, 10, 11]. Under this assumption, the spectra are perfectly reproduced with a single set of parameters for the magnetic field values of $\sim$4 T, $\sim$6 T (not shown) and $\sim$13.5 T: The quadrupolar coupling ν_Q=3.30±0.05 MHz, the asymmetry parameter η=0.1±0.1, and the total hyperfine magnetic shifts K_c=2.35±0.15 % and K_{ab}=3.95±0.10 % (with respect to the resonance frequency of ^{59}Co nuclei with $\gamma = 10.03$ MHz/T). Each of these parameters, including the linewidth, is constant within error bars over the

entire T range explored (150-1.6 K).

K_{ab} and K_c are related to the orbital (χ^{orb}) and the spin (χ^{spin}) susceptibility through hyperfine couplings A^{orb} and A^{spin}. With the field aligned along α, the direction of a principal axis of both A and χ tensors,

$$K_{\alpha\alpha} = K_{\alpha\alpha}^{\text{orb}} + K_{\alpha\alpha}^{\text{spin}} = \frac{A_{\alpha\alpha}^{\text{orb}}}{g\mu_B}\chi_{\alpha\alpha}^{\text{orb}} + \frac{A_{\alpha\alpha}^{\text{spin}}}{g\mu_B}\chi_{\alpha\alpha}^{\text{spin}}. \quad (1)$$

$\chi_{\text{bulk}} = \chi^{\text{spin}}+\chi^{\text{orb}}+\chi^{\text{dia}}+\chi^{\text{imp}}$ (the last two terms stand for the diamagnetic and impurity contributions, respectively) was measured with a superconducting quantum interference device (SQUID) at a field of 1.45 T (Fig. 2). Below $\sim$70 K, χ_{bulk} shows a strong increase, the amplitude of which, unlike ^{59}K data, is sample dependent. The amplitude of this rise is also incompatible with ^{59}K data: With $^{59}A_{ab}^{\text{spin}} = 33$ kOe/μ_B [12], the error bars in $^{59}K_{ab}$ translate into a maximum possible variation $\Delta\chi \simeq 3\times10^{-4}$ emu/mol from 1.6 to 150 K. The stronger T dependence of χ_{bulk} at low T is thus attributed to magnetic impurities or defects. Subtracting a Curie contribution from the raw data restores the weak T dependence imposed by K data. There remains, however, some uncertainty as to the exact T dependence of the intrinsic χ: As seen in Fig. 2, subtraction of $\frac{0.0025}{T}$ and $\frac{0.0040}{T}$ terms (representing 0.7 and 1.1 % of S=1/2 moments, respectively) from χ_{bulk} results in clear differences below 10 K. Furthermore, the 18% of H1-3 phase, while not expected to qualitatively influence the discussion, may still slightly affect χ_{bulk}. Despite these uncertainties the data reveal that the spin susceptibility of CoO$_2$ possesses at most a modest T dependence (if any). A typical $\chi_{\text{spin}} = \frac{c}{T+\theta}$ dependence is ruled out, unless unrealistic values of both χ_{orb} and θ are used.

An average $\chi^{\text{spin}} \simeq (5\pm1)\times10^{-4}$ emu/mol is estimated after subtracting $\chi_{\text{dia}}+\chi_{\text{orb}} \simeq 2\times10^{-4}$ emu/mol [10, 13] from χ_{CoO_2}. χ_{spin} is thus enhanced by a factor $\sim$3.6 over the value for non-correlated electrons $\chi_0 = 2\mu_B^2 N(E_F)$, using the LDA-calculated $N(E_F) = 4.3$ eV^{-1} [3]. In dynamical mean-field theory (DMFT) calculations by Merino et $al.$ for the triangular Hubbard model, an enhancement factor $\frac{m^*}{m} \simeq 3.6$ corresponds to $U/|t| = 9-10$ and $x \simeq 0 - 0.05$ electron density [4]. This suggests the proximity of CoO$_2$ to the Mott insulator transition.

Compared to Na$_{0.3}$CoO$_2$, where χ is also weakly T dependent without Curie-Weiss behavior, χ_{spin} in CoO$_2$ is larger by about 2×10^{-4} emu/mol [13]. CoO$_2$ might thus be regarded as a Pauli paramagnet with χ^{spin} enhanced by electron correlation with respect to $x = 0.3$. One should, however, keep in mind that χ_{spin} is not the most sensitive quantity for discriminating between various physical descriptions. Antiferromagnetic (AF) correlations in a triangular lattice lead to a weak T dependence of χ^{spin}, even when moments are localized, and χ^{spin} is almost identical in a large T range on both sides of the Mott transition [14]. Actually, spin-lattice relax-

ation rate $(1/T_1)$ data shall establish the correlated-metal nature of CoO_2.

^{59}Co T_1 measurements were performed at the $H\|ab$ position of the central line, and at two magnetic field values: 5.2 and 13.3 T. These experiments probe different ratios of the main to secondary signal amplitudes. Almost identical results in all the measurements ascertain that the data are intrinsic to the CoO_2 phase, with no significant contamination from the secondary signal. T_1 values were extracted from fits of the recovery curves to the appropriate formula for magnetic relaxation. There is some distribution of T_1 values due to mixed contributions from different orientations, as is unavoidable in a random powder. This can be phenomenologically accounted for by a stretched exponent β in the fit of the recovery curves [15]. The fit gives $\beta \simeq 0.85 \pm 0.05$, not far from the single-component value $\beta = 1$. This is not surprising since the well-defined $H\|ab$ singularity of the central line largely dominates the total NMR intensity at this position on the spectrum. The obtained T_1 values, identical within errors to those obtained with $\beta = 1$, are marginally affected by the distribution. More importantly, this latter is also strictly T independent, hence it does not affect the obtained T dependence of T_1 at all.

Let us recall that T_1^{-1} is a measurement of low-energy spin fluctuations summed over all wave vectors, with a weighting factor $A(q) = \sum A^{\mathrm{spin}}(r)e^{i\vec{q}.\vec{r}}$:

$$(T_1 T)^{-1} = \frac{\gamma_n^2 k_B}{\mu_B^2 \hbar} \sum_{q, \alpha \perp H} |A_{\alpha\alpha}(q)|^2 \frac{\chi''_{\alpha\alpha}(q, \omega_n)}{\omega_n} \quad (2)$$

Above $T^* \simeq 7$ K, a fit of $(T_1 T)^{-1}$ data to $(\frac{a}{T+\theta})^\alpha$ leads to $\theta = 94 \pm 31$ K and $\alpha = 0.92 \pm 0.20$. The data thus favor $\alpha = 1$, predicted *e.g.* for 2D nearly AF metals [16]. $\alpha = 3/2$ for 2D nearly ferromagnetic metals [16] is ruled out while $\alpha = 3/4$ calculated for itinerant electrons in a frustrated 3D lattice [17] cannot be excluded. The data also indicate that any additional T independent contribution to $(T_1 T)^{-1}$, such as orbital relaxation, has to be smaller than 3 s^{-1} K^{-1}. The absence of any marked T dependence of the $q = 0$ part of χ'_{spin}, while spin fluctuations are evident from the Curie-Weiss behavior of $(T_1 T)^{-1}$, indicate that spin fluctuations in CoO_2 are not ferromagnetic: Correlations at $q = 0$ should show up in an increase of $\chi_{\mathrm{spin}}(q = 0)$ with decreasing T. As a matter of fact, an identical (Curie-Weiss) T dependence of both K_{spin} and $(T_1 T)^{-1}$ is observed in ferromagnetically correlated metals such as $Sr_{1-x}Ca_xRuO_3$ [18] or $Na_{0.72}CoO_2$ [19].

Magnetic correlations in CoO_2 are (qualitatively) reminiscent of $Na_{0.3}CoO_2 \cdot yH_2O$ [9, 11] and of the 2D metal with an anisotropic triangular lattice κ-$Cu[N(CN)_2]Br$ [14]. CoO_2, however, shows neither a magnetic nor a superconducting ground state: the clear saturation of $(T_1 T)^{-1}$ below $T^* \simeq 7$ K (Inset to Fig. 2c) suggests that the Korringa law $K^2 T_1 T$=constant holds,
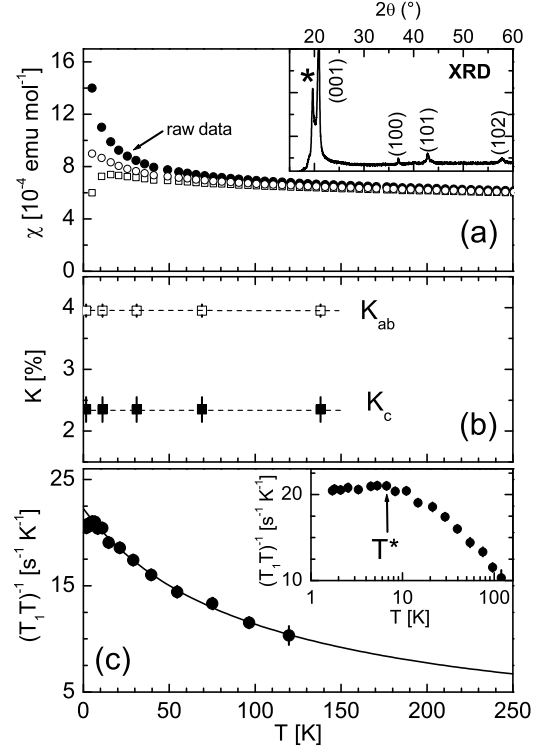

FIG. 2: (a) SQUID raw data (dots). Open circles and squares are obtained by subtracting impurity terms $\frac{0.0025}{T}$ and $\frac{0.004}{T}$, respectively, from the raw data (see text). Inset: XRD data for the O1 CoO_2 phase. The peak marked by a star is attributed to the Li-rich H1-3 phase [7]. (b) ^{59}Co hyperfine shifts K for $H\|ab$-planes and $H\|c$-axis with dotted lines to guide the eye. (c) ^{59}Co $(T_1 T)^{-1}$ data and fit to the $\frac{2200}{T+100}$ dependence. Inset: The same data in log horizontal scale.

thereby pointing to a Fermi-liquid regime at low T. In this regime, a classical criterion for ferromagnetic (resp. AF) correlations is provided by the value $R < 1$ (resp. $R > 1$) of the modified Korringa ratio $\mathcal{R} = (\frac{\gamma_e}{\gamma_n})^2 \frac{\hbar}{4\pi k_B}(K_{\mathrm{spin}}^2 T_1 T)^{-1}$ [20]. In principle, this analysis should consider separately the different hyperfine contributions, with possible correction factors to $\mathcal{R}$, such as for example $F_{\mathrm{cp}} = \frac{1}{3}f^2 + \frac{1}{2}(1 - f^2)$ for the core polarization (with f=1 for empty e_g orbitals as in our case) [20]. The mechanisms of hyperfine interaction for ^{59}Co in the cobaltates are, however, presently not known, making it impossible to disentangle the various contributions.

Separate analysis of $H\|ab$ and $H\|c$ contributions to $\mathcal{R}$ was not possible in the random powder. However, since K_{ab} is always larger than K_c in Na_xCoO_2, the ratio $(\frac{\gamma_e}{\gamma_n})^2 \frac{\hbar}{4\pi k_B}((K_{ab}^{\mathrm{spin}})^2 T_1 T)^{-1}$ is a lower bound for $\mathcal{R}$. According to the x-dependence of K_{ab}^{orb} revealed by Mukhameshin *et al.* [10], K_{ab}^{orb} should be larger than 3.44% in CoO_2 (minimum K_{ab}^{orb} value within error bars for the most magnetic $Co^{+3.7}$ site, corrected for the different shift reference [10]). This implies $K_{ab}^{\mathrm{spin}} \leq 0.61\%$, and

thus $\mathcal{R} \geq 2.7$. Alternatively, estimating $K_{ab}^{\mathrm{spin}} \simeq 0.3$ % from Eqn. 1 with $^{59}A_{ab}$=33 kOe/μ_B [12] and $\chi^{\mathrm{spin}} \simeq 5 \times 10^{-4}$ emu/mol, would lead to $\mathcal{R}$=11. This analysis thus confirms the "antiferromagnetic" (*i.e.* $q \neq 0$) character of spin correlations in CoO_2.

Finite-q spin fluctuations and low T Korringa behavior are again reminiscent of $Na_{0.3}CoO_2$, the lowest-x material whose magnetic properties have been reported so far [9, 19]. The reduced energy scale $T^* = 7$ K in CoO_2, however, contrasts with $T^* \simeq 80\pm10$ K in $Na_{0.3}CoO_2$ [9]. Even if T^* might not be proof of a canonical Fermi-liquid state [2], we interpret the reduced screening temperature T^* in CoO_2 as an increase of electronic correlations as $x \to 0$. Interestingly, Kondo screening of AF spin fluctuations is consistent with DMFT calculations for the triangular lattice in the vicinity of the Mott-insulator transition [4].

At this point, it must be stressed that we have obtained consistent results from several CoO_2 samples, prepared with the cleanest possible (electrochemical) method. We also recall that X-ray data rule out any residual amount of Li^+ larger than a few %, since these would not be accommodated by the specific $x = 0$ structure (which phase separates with the $x = 0.12$ phase) [21]. So, the magnetic properties revealed here for the first time (low T crossover towards a Fermi liquid ground state with screened spin fluctuations) are intrinsic to CoO_2. This behavior, so far unobserved in other members of the Na_xCoO_2 family, thus constitutes an important piece of the cobaltate puzzle.

We do not claim, however, that the actual CoO_2 material represents ideally undoped Co^{4+} planes. The possibility that oxygen vacancies make the system electronically equivalent to $x \neq 0$ must be considered. The questions of O vacancies and of the cobalt oxidization state are controversial in Na_xCoO_2 [6, 10, 22, 23, 24], so they can hardly be addressed in CoO_2 which is unstable in air and a more complex electrode material. Nevertheless, we recently obtained similar T_1 data in another compound with identical CoO_2 layers and a cobalt nominal valence also equal to +4 [12]. The consistency between these two studies together with the reproducibility of the results in several CoO_2 samples strongly suggest that Co ions are as oxidized as they can be in these materials. Furthermore, from the magnetic point of view, each O vacancy suppresses pathways for the Co-Co superexchange. In a correlated system with T dependent $\chi(q)$, such a strong perturbation should cause a T-dependent distribution of the local spin polarization [25]. Therefore, the striking absence of NMR line broadening on cooling is inconsistent with a large amount of O vacancies in our CoO_2 samples. Hence, the Co oxidization state should be close to +4 within a few %. Note, however, that this is an effective valence: Most of the difference between $x = 0.3$ and $x = 0$ compounds may actually occur in the oxygen band since there is evidence that the oxygen character of

the electronic density increases as $x \to 0$ [6, 19, 26, 27].

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